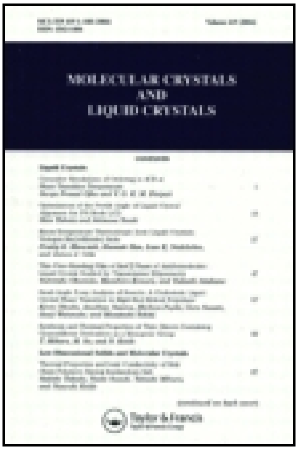

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Density Studies on Two Homologues of α,ω-Bis(4-n-Alkylanilinebenzylidine-4′-Oxy) Alkanes

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Density Studies on Two Homologues of α,ω-Bis(4-n-Alkylanilinebenzylidine-4′-Oxy) Alkanes

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α,ω-bis(4-n-alkylanilinebenzylidine-4′-oxy)alkanes exhibit a rich smectic polymorphism. We have studied the variation of density as a function of temperature across the phase transitions in two compounds of the series viz., 7.O4O.7 and 7.O5O.7. Both of these compounds exhibit a rare phase transition of Sm A – Sm F. The results confirmed first order nature of the transitions of Isotropic – Sm A and Sm A – Sm F, but with a smaller jump than expected in density as compared to monomers across the transitions. The estimated pressure dependence of transition temperature is also reported. The results are discussed in the light of available literature data.

Keywords: Schiff base dimers; Isotropic – Smectic A transition; Sm A-Sm F transition; density jump

INTRODUCTION

Liquid crystal dimers differ from conventional low molar mass mesogens in that they are composed of molecules, in which two anisotropic groups are linked by a flexible spacer. They have been attracting a great deal of interest in recent years not only from their ability to act as model compounds for semi-flexible main-chain liquid crystal polymers but also because they show quite different properties to conventional low molar mass liquid crystals. The liquid crystalline properties as well as the structure of the different liquid crystal phases of these compounds are found to be dependent on the number of carbon atoms in the spacer[1-9].

α,ω-bis(4-n-alkylanilinebenzylidine-4'-oxy) alkanes (hereafter referred to as m.OnO.m) homologous series of compounds have shown a rich smectic mesomorphism[1]. In addition to the commonly observed smectic A, smectic C, smectic B phases, the uncommon smectic F phase is also present in a number of long terminal chain length homologues. Many of the transitional properties of these dimers depend strongly on the length and parity of the spacer. In particular, the Nematic-Isotropic transition temperatures and entropies exhibit a marked alternation on increasing the spacer length. This alternation of Nematic – Isotropic transition is attenuated as the length of the spacer increases, whereas the entropy change at the transition, $\Delta S/R$, exhibits the same striking alternation but now there is little indication that this alternation decreases with spacer length. These compounds exhibit quite interesting structural features in that the X-ray diffraction studies have shown an unusual feature in the diffraction pattern for the smectic F phases exhibited by odd-membered compounds[1,5]. This feature is an unresolved shoulder on the peak in the wide-angle region, which has not previously reported and may arise from a distortion of the hexagonal lattice due to the difficulties in packing of bent molecules.

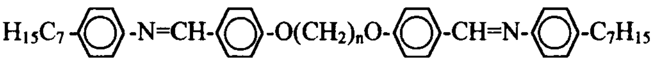
It is interesting to note that smectic phase formation for these dimers involve, microphase separation into three regions viz., mesogenic groups, terminal chains and spacers each constituting a microphase. In contrast, monomers have only two regions viz., mesogenic groups and terminal chains. As a part of our systematic study of rare phase transitions, we present here the density studies on two compounds of the m.OnO.m homologous series. These are 7.O4O.7 and 7.O5O.7 both of which exhibit Isotropic – Smectic A and the rare Smectic A – Smectic F phase transitions. The Smectic A – Smectic F transition is monotropic in 7.O5O.7, while it is enantiotropic in 7.O4O.7.

EXPERIMENTAL

The compounds were synthesized using the procedure given in literature[1] and repeatedly recrystallized from ethyl acetate until the transition temperatures were reproducible. The Differential Scanning Calorimetry (DSC) studies were carried out on Perkin-Elmer DSC7. Various phases exhibited by the compounds were characterized by observing their textures under a polarizing microscope attached with an indigenous hot stage. The temperature resolution of the microscopic observations was 0.1°C. Density studies were carried out with a bicapillary pyknometer[10]. The diameter of the capillary was about 0.35 mm and the accuracy in the density measurements was ±0.1 Kg. m^{-3}. The permitted cooling rate in the experiment was 2°C hr^{-1} and the temperature accuracy is ±0.1°C.

RESULTS AND DISCUSSION

The molecular structure of the compounds and phase transition temperatures are shown below.



7.O4O.7 (n=4) and 7.O5O.7 (n=5)

$$\begin{tikzcd}
7.O4O.7 & K \arrow[r, leftrightarrow, "112.1^{\circ}C"] & S_F \arrow[r, leftrightarrow, "167.6^{\circ}C"] & S_A \arrow[r, leftrightarrow, "212.1^{\circ}C"] & I
\end{tikzcd}$$

$$\begin{tikzcd}
7.O5O.7 & K \arrow[r, "108.6^{\circ}C"] & S_A \arrow[r, leftrightarrow, "142.1^{\circ}C"] \arrow[d, "98.3^{\circ}C"] & I \\
 & & S_F \arrow[ul, "88^{\circ}C"'] &
\end{tikzcd}$$

DSC scans of 7.O4O.7 and 7.O5O.7 show sharp melting transition which is an indication of the purity of the compound. The transition temperatures and entropy change at different transitions are in excellent agreement with reported literature values[1].

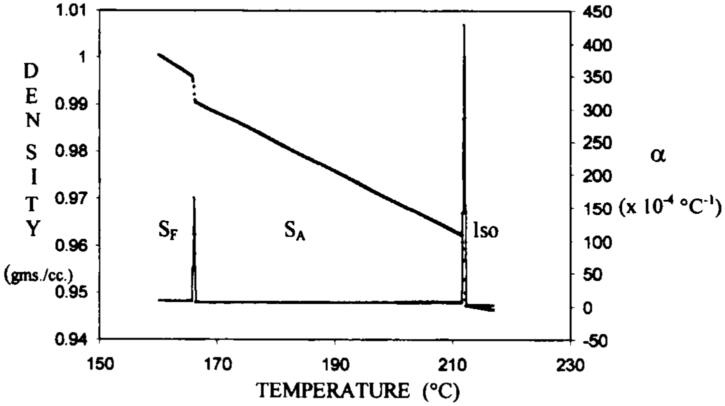


FIGURE 1 Density and Thermal Expansion Coefficient variation with temperature in isotropic, smectic A and Smectic F phases of 7.04O.7

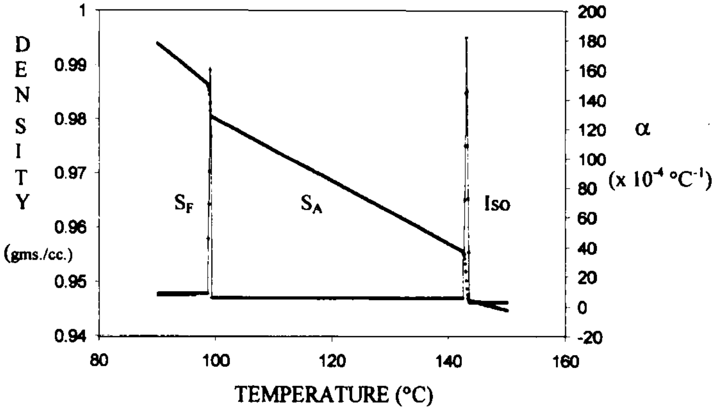


FIGURE 2 Density and Thermal Expansion Coefficient variation with temperature in isotropic, smectic A and smectic F phases of 7.05O.7

The variation of density as a function of temperature and the variation of estimated thermal expansion coefficient (α = dlnV/dT where V is molar volume) with temperature for 7.O4O.7 and 7.O5O.7 are shown in figures 1 and 2 respectively. In both compounds, the density increases as the temperature decreases, except in the vicinity of the phase transitions. The molar volume of 7.O4O.7 at T_{AI}+5°C was found to be 681.50 x 10^{-6} m^3 mol^{-1} whereas the molar volume of 7.O5O.7 at T_{AI}+5°C was found to be 697.01 x 10^{-6} m^3 mol^{-1}. Therefore, the increment in molar volume per methylene unit is 15.50 x 10^{-6} m^3 mol^{-1}, which is in agreement with the literature data[11].

The Isotropic – Smectic A transition in both 7.O4O.7 and 7.O5O.7 is inferred as a first order transition with a significant jump in density as well as indicated by a peak in thermal expansion coefficient. Further, coexistence of isotropic and smectic A phases is observed for 0.6°C in 7.O4O.7 and for 0.9°C in 7.O5O.7. However, significant jump in density at the transition is completed within 0.2°C in 7.O4O.7 and 0.3°C in 7.O5O.7. The observed density jump ($\Delta\rho/\rho$ %) across the I – S_A transition is 1.57% in 7.O4O.7 and 0.95% in 7.O5O.7 and is in agreement with the reported values[12]. These density jumps and a thermal expansion coefficient peak value of 428 x 10^{-4} °C^{-1} for 7.O4O.7 and 182 x 10^{-4} °C^{-1} for 7.O5O.7 confirms the I-S_A transition to be first order transition. The minimum and maximum values of density change reported so far across I – S_A transition are 0.35% and 2% respectively. However, the density jump across the I – S_A transition in both of these compounds is significantly smaller than that for the transition exhibited by monomers. This is quite unexpected since the entropy change at I – S_A transition in 7.O4O.7 and 7.O5O.7 is much higher compared to that of monomers. A comparison of density jumps and transition enthalpy at I-S_A transition in different compounds (monomers) and dimers is presented in Table 1.

In compounds exhibiting two phase transitions separated by a narrowtemperature range, large density jumps are observed in some compounds at the phasetransition on the high temperature side. Analogous results[13,14] are observed at Nematic – Smectic A transition also in the compounds exhibiting narrow nematic phase. In the present study, presumably, large smectic A phase thermal range of 46.8°C in 7.04O.7 and 44.2°C in 7.05O.7 is responsible for smaller density jumps at the I – S_A transition although the enthalpy change at the transition is significantly higher.

TABLE 1 Density jump and heat of transition at I-S_A transition of some compounds.

COMPOUND	$\Delta\rho/\rho$%	ΔH/J mol^{-1}	References
7.04O.7	1.57	17665.73	Present work
7.05O.7	0.95	9046.68	Present work
Di-n-hexadecyl 4,4'-azoxy cinnamate	0.40	4764	13
Di-n-undecyl 4,4'-azoxy cinnamate	0.35	5555	13
Di-n-undecyl 4,4'-azoxy-α-methyl cinnamate	1.21	8565	13
n-amyl-4(4-n-dodecyloxybenzylidene amino) cinnamate	1.28	8414	13
N-(4-n-Heptyloxybenzylidene)4'-n-octylaniline	1.04	5870	15
N-(4-n-octyloxybenzylidene)4'-n-butylaniline	1.11	5680	14
Terephthalylidene-bis-p-n-decylaniline	1.82	7080	12
Terephthalylidene-bis-p-n-octylaniline	0.96	5670	16
Di, ethyl 4,4'-azoxy dibenzoate	2.00	5442	17

An estimate of the pressure dependence of transition temperatures can be obtained using Clausius-Clapeyron equation

$$\frac{dT_t}{dP} = T_t\left(\frac{\Delta V}{\Delta H}\right)$$

where T_t - Transition temperature.
ΔV - Molar volume change associated with the transition.
ΔH - Heat of transition.

The estimated values of the pressure dependence of transition temperatures and the molar volume changes along with I-S_A transition temperature are presented in

Table 2. The estimated value of pressure dependence of transition temperature from the molar change and heat of transition (dT_t/dP) is 29.08 K/k bar for 7.O4O.7 and 30.07 K/k bar for 7.O5O.7. These values are in reasonable agreement with reported values estimated for I – S_A transition in monomers.

The smectic A – smectic F transition is inferred by a large jump in density in both 7.O4O.7 and 7.O5O.7 compounds. The observed density jump is 0.55% in 7.O4O.7 whereas 0.62% in 7.O5O.7. These density jumps along with the thermal expansion coefficient peak value of 165 x 10^{-4} °C^{-1} for 7.O4O.7 and 160 x 10^{-4} °C^{-1} for 7.O5O.7 at the transition confirm S_A – S_F transition as first order transition. Smectic A – Smectic F transition is an example of a transition from disordered orthogonal structure in smectic A to the ordered smectic F phase in which the molecules are packed in layers with a pseudo-hexagonal arrangement with a two-dimensional structure of the positional order and long axis tilted (direction of tilt is towards an edge of hexagon) with respect to the layer planes (i.e., with uncorrelated layers but long range bond orientational order) is expected to be a first order transition. This transition is observed very rarely. The only other compound on

TABLE 2 I-S_A transition temperature, heat of transition and pressure dependence of transition temperatures

COMPOUND	T_{AI}/°C	ΔH/J mol^{-1}	dT_t/dp (K/k bar)
7.O4O.7	212.1	17665.73	29.08
7.O5O.7	142.1	9046.68	30.07
Di-n-hexadecyl 4,4'-azoxy cinnamate	135	4764	26.7
Di-n-undecyl 4,4'-azoxy-α-methyl cinnamate	85.7	8565	18.9
n-amyl-4(4-n-dodecyloxybenzylidene amino) cinnamate	137.2	8414	33.7
N-(4-n-Heptyloxybenzylidene)4'-n-octylaniline	83	5870	27.3
N-(4-n-octyloxybenzylidene)4'-n-butylaniline	81.2	5680	26.5
Terephthalylidene-bis-p-n-decylaniline	190.2	7080	72.2
Terephthalylidene-bis-p-n-octylaniline	202.4	5670	42

which density studies were reported across smectic A – smectic F transition is N(p-n-nonyloxy benzylidene)-p-n-Butylaniline (9O.4) in which a density jump of 1.42% was observed[18]. The estimated pressure dependent transition temperature is found to be 37.25 K/k bar for 7.O4O.7 and 16.82 K/k bar for 7.O5O.7. These values are smaller than that reported for 9O.4 which is 48 K/k bar[18]. Significantly, smaller density jumps observed for 7.O4O.7 and 7.O5O.7 compared to monomer ($\Delta\rho/\rho\%$ = 1.42 for 9O.4) may be assigned to the large volume of dimer molecule compared to that of monomer.

ACKNOWLEDGEMENTS

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